Indian J. Phys., **52A**, 345–358 (1978)

NMR investigations of phenanthrenquinone and benzil

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(*Received* 2 *August* 1977)

Low resolution NMR investigations of phenanthrenequinone and benzil were made in the temperature range (77–480)K and (77–367)K respectively The lattice of phenanthrenequinone was found rigid at 77K At 313K, the sudden drop of second moment from the rigid lattice value ($10{\cdot}98 \pm 1$ G^2) to the value ($5{\cdot}26 \pm 1$ G^2) was explained as due to the molecular reorientation about the diad axis along its length. The activation energy for the motion was obtained to be 8·5 KCal/mole The theoretical rigid lattice value of second moment for benzil ($11{\cdot}47$ G^2) agreed with the experimental value ($12{\cdot}01 \pm 1$ G^2) at 77K The torsional oscillations are found to exist up to 197K At 298K second moment falls to value ($7{\cdot}78 \pm 1$ G^2) which was attributed to the rotation of both the phenyl groups about the axis of symmetry of the group passing through $C(0)$-$C(1)$ and $C(0')$–$C(1')$ bonds. The potential barrier to the rotation was found to be 2·1 KCal/mole The further fall of second moment after 319K up to m p is suggested owing to the slow reorientation of phenyl groups about $C(0)$–$C(0')$ bond. The potential barrier for such a free rotation was estimated to be ~2.1 KCal/mole which is only partially approached in the crystalline phase of benzil

1 Introduction

The NMR spectroscopy is of great value in the structural investigations as the proper interpretation of spectrum yields significant informations about the environment of the nucleus under study Presently studied phenanthrenequinone and benzil have same carbon skeletons but different number of protons and under specific dehydrogenation benzil cyclizes into phenanthrenequinone. Both undergo benzil—benzilic acid type of rearrangement (Hodge 1971) and photo-chem behaviour study of Gream (1969) has attributed them somewhat similar character The two ketone groups in phenanthrenequinone are tied to rigid C–C bond but in benzil to roomier C(0)–C(0′) bond which explains why common nucleophile attack is more feasible in benzil as compared to former. Present investigations of phenanthrenequinone show that the molecule reorients about the diad axis along its length maintaining the permanent cis arrangement with two ketonic groups always in the same side. The two phenyl groups in benzil molecule are found to rotate about the symmetry axis of the group, but as the temperature approaches the melting point (368°K), slow reorientation of phenyl groups about C(0)–C(0′) bond also starts i e. from cis to trans mode

[figure 3(a) & (b)] which further facilitates the nucleophilic addition property. The NMR spectral features of the two compounds are quite different which is in accordance with the marked quinonide structure of phenanthrenequinone and the ketonic one of the benzil.

2. Crystal Structure

2.1 9,10 *Phenanthrenequinone*

The crystal structure of 9,10-phenanthrenequinone was determined by Allegaune *et al* (1961). There are eight molecules in the unit cell. The crystalline system is monoclinic and the unit cell has parameters: $a = 12{\cdot}60 \pm 0{\cdot}03$ Å, $b = 10{\cdot}44 \pm 0{\cdot}02$ Å and $c = 14{\cdot}20 \pm 0{\cdot}03$ Å with $\beta = 92° \pm 1'$. The space group is $C2/c$. Caldwel & Fevre (1939) suggested that the angle Ph–C – O and Ph–C C are 120° and the two Ph CO group lie in the planes that make an angle of 90°–100° with each other. The side rings in phenanthrenequinone have been shown to be approximate benzene nuclei from L C A O and U V studies of Akuta (1959) in the 200–600 mμ region. The two rings at either extremity are slightly displaced in opposite directions. All the intermolecular distances correspond to normal Van der waals interaction. The molecular model of phenanthrenequinone is shown in figure 1. The inter ring C C distances and valency angles of Trotter (1963) for phenanthrene are taken. C-H and C – O bond lengths are assumed to be 1·08 Å and 1·32 Å respectively.

2.2 *Benzil*

Brown & Sadanga (1965) have determined the crystal and molecular structure of benzil by X-ray powder diffraction. The unit cell contains three molecules and lattice constants are. $a = 8{\cdot}376 \pm 0{\cdot}009$ Å and $c = 13{\cdot}700 \pm 0{\cdot}008$ Å. The space group of the crystal is one of the enantiomorphic pair $P3_121$ and $P3_221$. The molecules lie with their midpoint on the crystallographic two fold axis of symmetry (Banerjee 1938). The defect structure in crystal of benzil was observed by Harold (1971). The molecule has skew configuration (Bernal 1963, Knaggs 1939, Gibling 1942) and two PHCO halves lie in different planes. Nonplanarity of CO groups was observed by Subrahmanyam (1964) and Davydov (1965) also noticed that withdrawl from coplanarity of two CO groups. Though the two CO groups of benzil are independent, still a very weak interaction between them was observed by Brandt (1963) by NMR and U V techniques. Subrahmanyam (1964) had found that planes of aromatic rings are inclined to the braid axis by 14°.

3. Theoretical Calculations

3.1 *Rigid lattice second moment*

Vanvleck's theory (1948) for polycrystalline material having only a single species of magnetic nuclei at resonance provides for rigid lattice second moment.

This comprises of two parts (i) that due to intramolecular contribution and (ii) that due to the intermolecular contribution

(a) *Phenanthrenequinone*. The intramolecular contribution (S_1) to second moment in G^2 has been calculated using the expression

$$S_1 = \frac{6(I+1)}{5I} \gamma_p^2 N^{-1} \sum_{j\,k} r_{jk}^{-6} \qquad \ldots \quad (1)$$

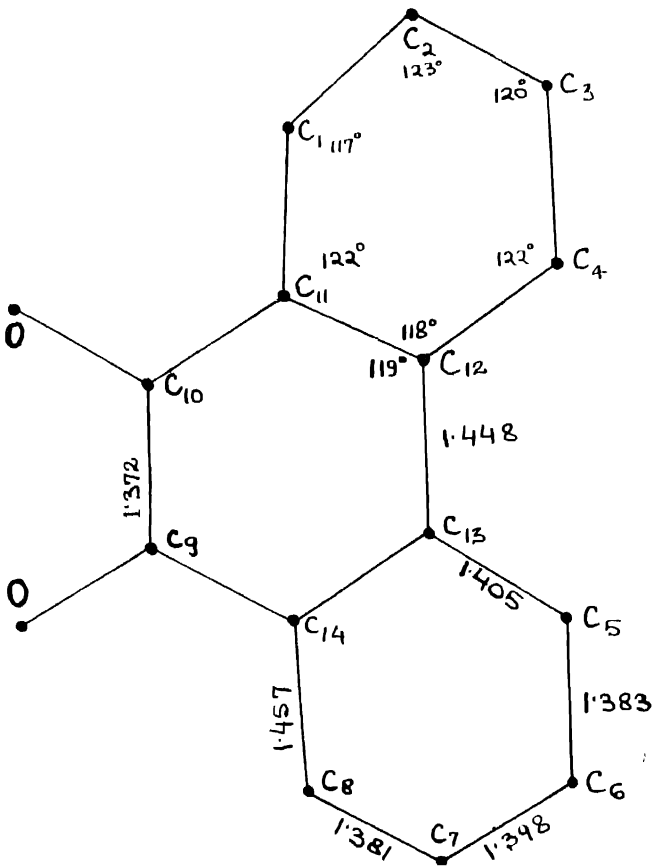

Fig 1. Molecular model of phenanthrenequinone; Bond lengths (A°) and valency angles (°).

where I is spin number of resonating nuclei, μ_p is the proton magnetic resonance and r_{jk} is the interproton distance between jth and kth nuclei On substituting the corresponding values of the quantities involved in eq (1), a rather simplified expression is obtained

$$S_1 = \frac{715{\cdot}9}{N} \sum_{j>k} r_{jk}^{-6}. \qquad \ldots (2)$$

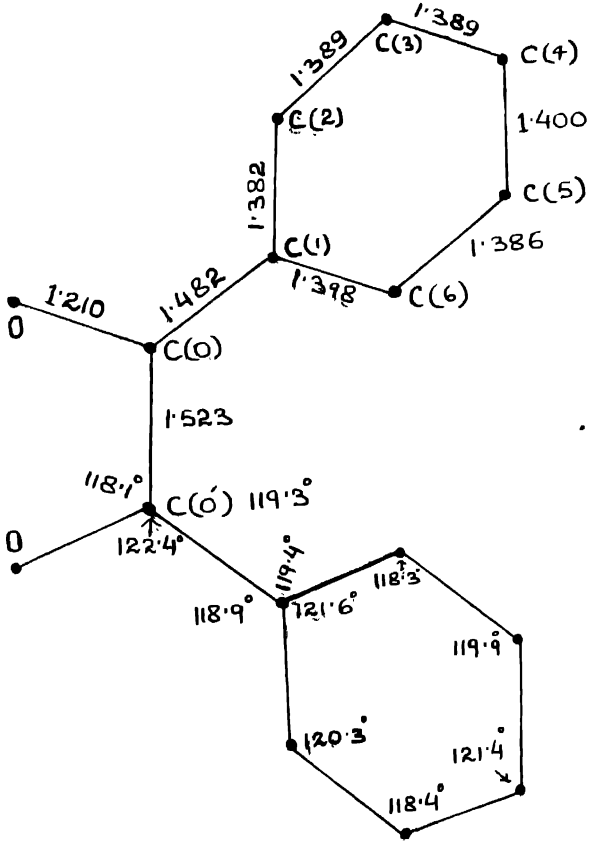

Fig 2 Bond lengths (A°) and interbond angles (°) in a Benzil molecule, C–H = 1 08 (assumed); cis mode

The evaluation of term $\sum_{j>k}$ was made by us by calculating the positional coordinates of H atom taking aid of some molecular data of phenanthrene The r_{jk} distance between different protons were then calculated The substitution in eq (2) yielded $S_1 = 4{\cdot}92\ G^2$.

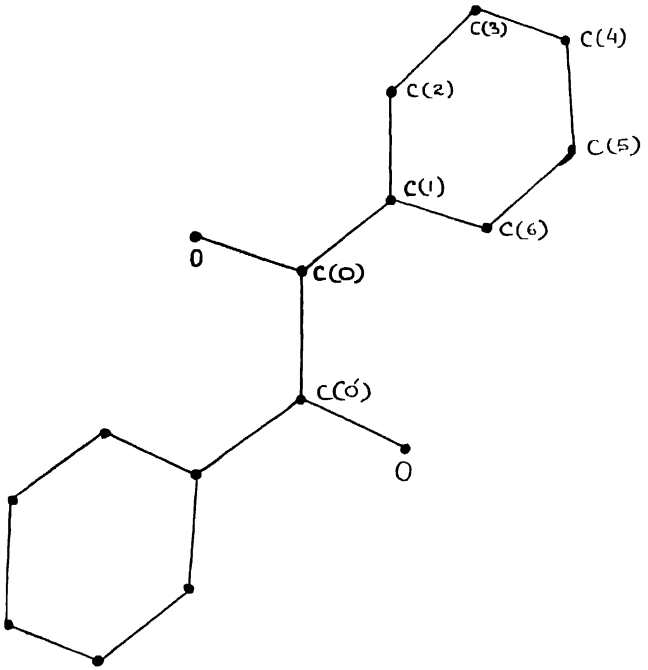

Fig. 3(a) Trans mode.

For intermolecular contribution (S_2), the method of Andrew & Eades (1953) was followed We estimated its value to be $6\ 70\ G^2$. This value appears quite reasonable as in case of acenaphthenequinone, a simular compound Agarwal & Gupta (1974) obtained this value to be $6{\cdot}32\ G^2$. It may be pointed out that the formula of Smith (1965) also gives for S_2 but it requires detailed knowledge of spatial depositions of atoms in the lattice

Adding up the two contributions, S_1 and S_2, the total rigid lattice second moment for phenanthrenequinone comes out to be $4{\cdot}92+6{\cdot}70 = 11{\cdot}62\ G^2$ which tallys with the experimental second moment at 77 K ($10{\cdot}98 \pm 1\ G^2$).

(b) *Benzil* : Authors (Mishra *et al* 1976) have calculated the rigid lattice second moment for benzil, previously The values of S_1 and S_2 are 5.37 G^2 and 6.1 G^2 respectively

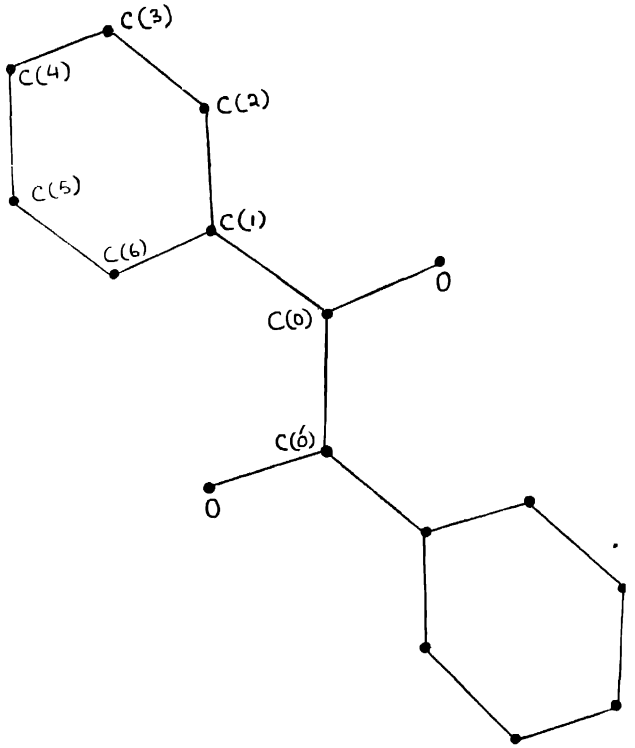

Fig. 3(b) Alternative trans mode

3.2 *Activation energy*

Gutowsky & Pake (1950) and, also, Kubo & Tomita (1954) modified the theory of Bloembergen *et al* (1948) The modified expression is obtained as

$$2\pi\nu_c = \alpha\gamma\delta H|\tan\{\pi(\delta H^2-B^2)/2(C^2-B^2)\}| \quad \ldots (3)$$

where ν_c is the correlation frequency for motion narrowing the spectrum line, C is the line width at temperature below the transition regon, B is the line width at temperature above the transition region, γ is the gyromagnetic ratio and α is a

constant. It is seen from the expression that at higher value of temperature, B is small and $(G^2 - B^2)$ may be taken as (G^2) approximately. The correlation frequency ν_c is assumed to obey the Arrhenius equation

$$\nu_c = \nu_0 \exp. \left[- \frac{E_R}{RT} \right] \qquad .. \quad (4)$$

where E_R is activation energy and R is gas constant/mole.

(a) *Phenanthrenequinone* The plot of log ν_c vs $1/T$ from eq (4) yielded a straight line and its slope thus gives activation energy for rotation. The activation energy to overcome the barrier to rotation came out to be 8·5 KCal/mole for phenanthrenequinone.

(b) *Benzil* The method discussed above was adopted and for Benzil the activation energy was found to be 2·1 KCal/mole.

3·3 *Calculation of reduction in second moment when molecule as a whole or group, reorients about an axis*

The effect of molecular rotation on the second moment of the absorption spectrum was studied by Gutowsky & Pake (1950). They have shown that in such a case the intramolecular contribution (S_1) is reduced by a factor

$$F = 1/4(3 \cos^2 \theta_{jk} - 1)^2$$

where θ_{jk} stands for angle between axis of rotation and the line connecting the jth and kth proton. The reduction in intermolecular contribution to second moment (S_2) brought about by rotation of molecule about symmetry axis was studied by Anfew & Eades (1953). Theory shows that S_2 reduces by a factor 0·24.

(a) *Phenanthrenequinone* : The structural considerations of phenanthrenequinone (figure 1) show that the molecule can reorient only about the diad axis along its length. For this mode of rotation space (as calculated) of radius of the order of 3·625 Å is required. The possibility of the rotation about two other diad axes perpendicular to length is not feasible because end-over-end turning requires, as calculated by us, a space of radius of the order of 9·226 Å. Thus for a reorienting molecule about the diad axis along its length, the intramolecular contribution was computed to be about $3{\cdot}00\ G^2$. The value of the intermolecular contribution for same mode of rotation came out to be $1{\cdot}62\ G^2$. The total value of second moment thus is, $3{\cdot}18 + 1{\cdot}62 = 4{\cdot}80\ G^2$.

(b) *Benzil* . There are three possible modes of rotation. (i) The reorientation of molecule about the crystallographic axis of symmetry, (ii) the reorientation about an axis passing through C(0)–C(0′) bond and lastly (iii) the rotation of phenyl groups about the symmetry axis of the group and the rotation of phenyl groups about C(0)-C(0′) bond.

The first mode appears to be not possible as it required larger amount of activation energy and space The melting point of benzil is less and space required was calculated to be 3·907 Å radius sphere The second mode of rotation is also not feasible for similar reasons and also on account of symmetry and equilibrium considerations For the third probability i e. rotation of phenyl groups about the symmetry axis of groups that passes through the C(0)–C(1) bond; the reduction in intramolecular contribution to second moment was calculated to be 3·24 G^2. The reduced intermolecular contribution to second moment was estimated according to method of Smith (1965) Smith has given a range of reduction factors of (0·65–0·50) for stationary rotating interactions and the range (0·42–0·25) for rotating—rotating interactions Since two phenyl groups are symmetrically attached with respect to crystallographic axis, their motion will be identical Thus considering the rotation of both the groups the intermolecular contribution will reduce in the range (2·54–1·52) G^2 and the S_2 will be in the range (3 54 -4 58) G^2. The total second moment would thus lie in the range (6·78–7·82) G^2 The observed value at room temperature was (7 78 ± 1) G^2 and thus confirms the hypothesis of the rotation of both the phenyl groups about symmetry axis as to maximise the distance between the protons The theoretical calculations for the reduction in second moment due to rotation of both the phenyl groups about C(0)–C(0′) bond could not be made for few reasons

4. Experimental Details

The NMR derivative traces were recorded at Tata Institute of Fundamental Research (Bombay) using a Varian Associates variable frequency broad line spectrometer and 12 inches magnet system The temperature monitoring was done by thermocouples using current of hot or cooled nitrogen and V-4340 variable temperature probe was used. 77°K study was made by using dewars of liquid nitrogen. The details of the spectrometer are given by Agarwal (1970)

The chemicals were of high purity and were further purified The accuracy in the measurement of experimental second moments from derivative traces was approximately ± 1·0 gauss

5. Experimental Results

The experimental second moments were determined from the derivative traces using the expression of trapezium rule For phenanthrenequinone the second moment vs temperature is plotted in figure 4 and figure 5 shows the variation of second moment with temperature for Benzil

6 Discussion

Phenanthrenequinone : In the present NMR analysis of phenanthrenequinone, the theoretically calculated value of the rigid lattice second moment, from the

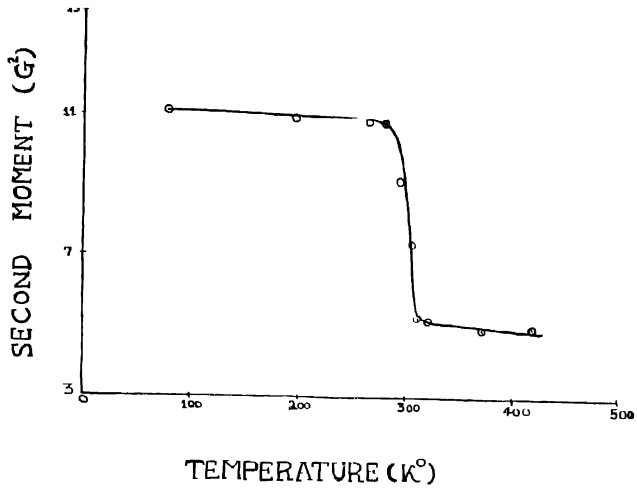

Fig. 4 Variation of second moment with temperature; (phenanthrenequinone, Crystal phase).

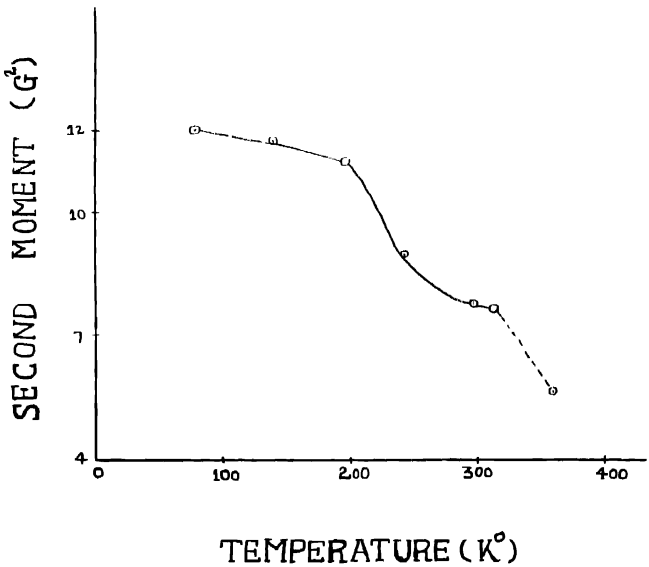

Fig. 5. Variation of second moment with temperature; (benzil, crystal phase).

model (figure 1), comes out to be 11·62 G^2. This value agrees favourably with the experimental second moment at 77°K (10·98±1 G^2). Thus shows that the assumed model is correct and the lattice is rigid at 77 K

The second moment remains practically constant upto 284 K Thus shows that molecular motions do not come into play up to this temperature Thereafter, the second moment decreases and suddenly drops to value 5·26±1 G^2 (figure 4) at 313 K which remains almost constant upto the melting point of the sample. This sudden drop suggests the onset of some sort of molecular motion The various possible modes of rotation of the molecule as a whole are discussed in sec 3 3(a) The reorientational second moment when molecule reorients about the diad axis along its length has been theoretically calculated to be about [sec 3 3(a)] 4·81 G^2. This value agrees reasonably with the experimentally obtained value 5·26±1 G^2. The activation energy for the reorientation of phenanthrenequinone molecule is obtained to be 8·5 KCal/mole The potential barrier is rightly overcome at a high temperature as 313 K

The dielectric studies of Robert (1958) in wavelength range (1·25–5·00 cm) at different temperatures show that the value of relaxation time for phenanthrenequinone is anomalously high They have explained it owing to the possibility of great volume swept out by the molecule in orienting about the axis along the length The theoretical study of NMR spectra in fused ring systems (Batterhann 1964) also includes the possibilities of specific transitions Kazakova (1962) and (1960) has shown from the analysis of E.P R. hyperfine structure that the stability of aromatic radical is increased by the delocalization of unpaired electron Jeanne (1957) emphasised that the polarity of C = O bond in polycyclic quinones has no homogeneous relation with the vibrational frequency Conductivity measurements (David 1960) and thermal transfer of images of phenanthrenequinone (Dupont 1965) show that the quantum yield of charge carriers is effected by radiations In solid state the magnetic susceptibility of phenanthrenequinone is high—10·5 units (Yoshio 1958) and Smirnov (1958) showed phenanthrenequinone to exhibit less inhabiting activity in thermopolymerisation of styrene

In systems of benzene nuclei arranged in straight chain, Magnus (1956) found that in traversing from a hydrocarbon to respective quinone, the resonance energy for aromatic double bonds were equal. Koutecky (1962) showed that in such a traversal (i e from hydrocarbon to respective quinone) the absorption band of electronic spectrum at longest wavelength is not much changed. A close correspondence in vibration frequency of phenanthrenequinone is observed to exist by Raman and I R study of Barua (1970) The high resolution NMR investigations by Bartle (1967) show that coupling constants in both phenanthrene and phenanthrenequinone are generally same (though C_9–C_{10} bond is characteristically different) A comparative study of the present wide line

NMR of phenanthrenequinone with that of phenanthrene shows that general absorption features are essentially same in both the cases. This gives one more aspect of traversal from a hydrocarbon to quinone.

It is quite likely that in a series of polycyclic quinones, in passing from one quinone to other with the difference of one cyclic group, a proportional change in NMR absorption, phase transition and in activation energy may be observed. This view is borne out from the studies of Emil (1962) of oxidation and reduction potentials of polycyclic quinones which is related to structure of the quinones.

Benzil: The theoretical rigid lattice second moment (11·47 G^2) agrees, within the extent of experimental error, with the experimentally observed value at 77 K (12·01±1 G^2). This shows that lattice is rigid at 77 K and all type of molecular motions are frozen at 77 K. This also confirms the X-ray structure.

As temperature increases the second moment decreases gradually. This happens upto 197 K. This portion of the S–T curve (figure 5) is possibly due to some kind of torsional oscillations. Thereafter, the second moment falls rapidly and has a value 7·78±1 G^2 at 298°K. This suggests that some sort of molecular motion or group rotation has started. The fall in second moment was attributed to the rotation of the two phenyl groups about the symmetry axis of each group which passes through C(0)–C(1) bond and C(0′)–C(1′) bond. The calculated reorientational second moment [sec. 3.3(b)] for this case lies in the range (6·68–7·82 G^2) which agrees fairly well with the experimental second moment 7·18±1 G^2, confirming our assignment.

After 298 K, the second moment remains practically constant over a very small region of temperature. As the temperature is increased beyond 310 K, the second moment falls considerably. The fall in second moment continues with the further temperature rise. This fall beyond 310 K is possibly due to the onset of rotation of phenyl groups about the C(0)–C(0′) bond i.e. gradually turning over from cis to trans orientation. In solid phase such type of rotation must be slow, because free rotation of this mode requires a high activation energy to surpass the potential barrier. Our cis-trans mode of rotation at higher temperatures (available in the present case) is confirmed from several studies given below.

The dynamical effects in benzil are observed by Harold (1971). In solid phase, the self diffusion activation energy (which is related to Debye temperature) is not approached in the permitted temperature region (Ostercherin 1971) and in liquid state (in hydrocarbon solvent) the emission spectra (Schoglova 1965) shows fine vibrational structure. The molecular thermal motion in benzil is shown to exist by Brown & Sadanga (1965).

Natalis (1965) observed a very intense peak for $C_6H_5^+$ in benzil by electron impact studies and he has shown a high value of heat of formation

(~300 KCal/mole) which is possible only in liquid state The slowly rotating phenyl groups (about C(0)–C(0′) bond) achieve, thus, sufficient energy for solvation, only in liquid state In a study (William 1963) of stereo-isomeric triplet states of benzil in solid state, the phosphorence spectrum contained two emitting species which were believed to be cis and trans isomeric triplets of benzil: a diketone. The presence of benzil is shown by Nicholas (1962) to facilitate the trans product in dimerisation of cyclopentadiene and in general it influences 3 cis isomeration, apart from dimmerisation (Giorgio 1964). Vincenz (1964) found that cathodic reduction of present compound to cis and trans isomers is temperature dependent. Caldwell (1939) suggested that in the stable configuration of benzil (in nonpolar solvents) the ketonic groups make rotational oscillations of low amplitude There occurs dipolar repulsion between the Ph-group and O-atoms which tends to a trans-cis structure. Gaines (1963) has shown that the electron affinity of phenyl radical is very high.

The diffuse X-ray studies of Lonsdale (1941, 1940) show that diffuse spot intensity for benzil is markedly influenced by temperature and the diffuse spot pattern disappears at liquid air temperature but enhanced at elevated temperature The size of pattern suggest that they have aroused from molecular origin but Darwin (1941) considered that this pattern is directly associated with the orientation of individual molecules and its units and the effects depend upon imperfections in the lattice by thermal agitation. Similar analysis (Luisa 1961) at various temperatures shows that the streaks become thinner at about 100°K, as the temperature decreases Such maxima are predicted in Born's theory and the vibrational spectrum has minimum frequency. The absorption curves in near U V. have been reported by Andrew (1957) and a similar depression in conductivity is also observed. The diamagnetic anisotropy of benzil is temperature dependent and changes considerably from 293°K towards higher temperature. Leela (1956) have pointed out an uncertain relation of this change with molecular motions. The Laue photographs (Sen 1954, 1953) are explained from thermal theories and agreable results are obtained. Chandrasekhar (1961) explained the O.R.D. results with the concept of resonance between the similar polarizable unit of each individual molecular unit.

The dielectric constant data of crystalline and molten benzil at various temperatures (Sainte 1928, Williams 1929) are marked by the dynamical aspects of benzil molecule. The Cotton-Moulton Constant in the magnetic double refraction of benzil varies with temperature (Salceaune 1932)—being unusually high in the range 333 K–343 K. In the range (278–308) K, λ and $n-1/d$ decreases, being minimum at 308 K; and in the range (368 K–393 K) further decrease in the parameters is observed (Mallemann 1927) where λ and $n-1/d$ have usual meaning in dielectric relaxation measurements The thermodynamical properties in the temperature range 298·5 K–318 K are also revealed by differential

vapour pressure studies of Roduca (1970) Raman scattering from powdered benzil show that the several lines have their counter part in the vibrational spectrum of C_6H_6 (Folke 1969)

The interpretation of the spectrum in the temperature range (298°K and onwards) in terms of cis-trans isomerism seems quite adequate Such an explanation is also offered to E S R spectrum of hydroquinone by Barbas (1967) They have given the value for potential barrier for the motion about C-O bond to be ~10 KCal/mole We have not calculated it for this case but reasonably estimate it to lie in the range (10–11 5) KCal/mole. In crystalline phase this value is only approached and the rotation is slow.

ACKNOWLEDGEMENT

Sincere thanks are due to Prof Vijayaraghavan and Dr L C Gupta (TIFR, Bombay) for the experimental facility Thanks are extended to Dr. B G. Gokhale, Head of the Department of Physics, University of Lucknow for his keen interest

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